

Estimation of Coupling Constants of a Three-Spin Chain: Case Study of Hamiltonian Tomography with NMR

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It has been shown that inter-spin interaction strengths in a spins-1/2 chain can be evaluated by accessing one of the edge spins only. We demonstrate this experimentally for the simplest case, a three-spin chain, with nuclear magnetic resonance (NMR) technique. The three spins in the chain interact through nearest-neighbor Ising interactions under site-dependent transverse fields. The employed molecule is an alanine containing three ¹³C nuclei, each of which has spin-1/2.

I. INTRODUCTION

Fabricating a quantum system that would perfectly function as we desire is very challenging. Even with the most advanced nanotechnology it is still difficult to build a structure that would have the exact values of system parameters to make it work as we initially designed. This gives rise to the crucial necessity of system identification. In the context of quantum control, the system identification primarily refers to the identification of the system Hamiltonian, also known as Hamiltonian tomography.

Yet, it is in general formidably hard to estimate the Hamiltonian: the number of necessary initial settings and measurements grows exponentially as the system size becomes larger. To make the problem of Hamiltonian estimation more feasible, various schemes to reduce the complexity and/or to minimize the effect of physical noise have recently been studied quite intensively. Examples are indirect, but efficient, schemes of Hamiltonian tomography of spin systems under limited access [1–5], and also an application of (classical) compressed sensing to the quantum setting [6, 7] that greatly reduces the overall complexity.

In the case of NMR, the interactions among spins in a molecule are usually determined by measuring all spins at once. But what if we are allowed to access only a single spin to reconstruct the whole Hamiltonian as in the above examples? In this paper, we report such an indirect Hamiltonian tomography of a three nuclei spin system with NMR as a minimum model. In the molecule, the spins effectively form a one-dimensional (1D) chain with nearest-neighbor interactions, which are of the Ising

type. We attempt to estimate the coupling constants by accessing solely the end spin pretending as if we had no knowledge about the interactions in advance. Then, we will make a comparison between the estimated coupling constants and the known values as estimated by standard methods.

The analysis that we carry out is different from that presented in [5, 8], where the coupling constants are estimated from the energy eigenvalues obtained from the spectral peaks, which are obtained from long time evolution of the spin at an end of the chain. In contrast, we obtain the coupling constants by fitting the time domain data without calculating the spectra in the present work. The materials presented in this paper therefore provide the first step toward the full verification of the scheme discussed in [5, 8]. While data fitting is not computationally efficient for large systems, we find that it is very suitable for the three-spin chain and more robust against relaxation than [5, 8]. Our finding thus paves the way to indirect estimation of a Hamiltonian of a small-scale noisy system where direct methods are not applicable. In such circumstances, it is impossible to obtain data over longer time periods, which is fundamental for obtaining sharp spectral peaks.

II. THEORY

In this section, we review how to estimate the spin-spin interaction strengths in a three-spin Ising chain with site-dependent transverse fields. The model in our mind is a three homonucleus molecule, such as alanine with three ¹³C nuclei. We use liquid-state NMR to control and measure the spins.

The initial state is, thus, a thermal state

$$\rho_{\text{th}}(T) = \frac{e^{-H_0/k_B T}}{\text{Tr}[e^{-H_0/k_B T}]}, \quad (1)$$

where

$$H_0 = -\omega_0 (I_z^1 + I_z^2 + I_z^3)$$

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with $I_i^1 = \frac{\sigma_i}{2} \otimes I \otimes I$, $I_i^2 = I \otimes \frac{\sigma_i}{2} \otimes I$, $I_i^3 = I \otimes I \otimes \frac{\sigma_i}{2}$. Here T is the temperature, ω_0 is the common Larmor frequency of the spins, and σ_i is the i th component of the Pauli matrices. We drop the interaction terms among spins and chemical shifts of the spins temporarily since they are small enough compared with ω_0 . We note that Eq. (1) is defined in the laboratory frame.

A weakly coupled system develops according to the Hamiltonian

$$\mathcal{H} = \omega_{11}I_x^1 + \omega_{12}I_x^2 + \omega_{13}I_x^3 + J_{12}I_z^1I_z^2 + J_{23}I_z^2I_z^3. \quad (2)$$

Here, ω_{1i} and J_{ij} characterize the transverse field of spin i and the coupling constant between spins i and j , respectively. We note that the Hamiltonian (2) is described in the rotating frames fixed to each spin.

Now we evaluate the dynamics of spin 1

$$M_k(t) \equiv \langle I_k^1(t) \rangle = \text{Tr}[\rho(t)I_k^1], \quad (3)$$

where $k \in \{x, y, z\}$ and

$$\rho(t) = (e^{-i\mathcal{H}t})\rho_{\text{th}}(T)(e^{-i\mathcal{H}t})^\dagger \quad (4)$$

is the density matrix of the system at time t .

The dynamics of spin 1 without relaxations nor transverse field inhomogeneities is calculated and shown in Fig. 1 when $\omega_{1i}/(2\pi) = 27$ Hz for all $i = 1, 2, 3$. The coupling constants $J_{12}/(2\pi) = 53.8$ Hz and $J_{23}/(2\pi) = 34.8$ Hz are taken from [9] as an example.

It is clear that Fig. 1 is far from reality. We then include the effects of transverse relaxations via the operator sum representation $\varepsilon(\rho) = \sum_{i=0}^3 E_i^\dagger \rho E_i$ where $\sum_{i=0}^3 E_i^\dagger E_i = I$ [10, 11]. We take

$$\begin{aligned} E_0 &= \sqrt{\lambda_0} I, \\ E_i &= \sqrt{1 - \lambda_i} (2I_z^i) \quad (i = 1, 2, 3), \end{aligned}$$

where

$$\begin{aligned} \lambda_0 &= \frac{1}{2}(-1 + e^{-t/T_2(1)} + e^{-t/T_2(2)} + e^{-t/T_2(3)}), \\ \lambda_i &= \frac{1}{2}(1 + e^{-t/T_2(i)}) \quad (i = 1, 2, 3), \end{aligned}$$

to represent the transverse relaxations.

Finally, we take into account the inhomogeneity of the transverse fields $\omega_{1i}(x)$ as a function of position x . We assume that the inhomogeneity has a Gaussian distribution

$$P(\omega_{1i}(x)) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(\omega_{1i}(x) - \omega_{1i})^2}{2\sigma^2}\right] \quad (5)$$

with variance σ to be determined later.

The coupling constants are estimated by comparing the spin dynamics obtained numerically with various pairs (J_{12}, J_{23}) with the experimental data. Both the effects of the relaxations and the field inhomogeneity are taken into account in the numerical calculation.

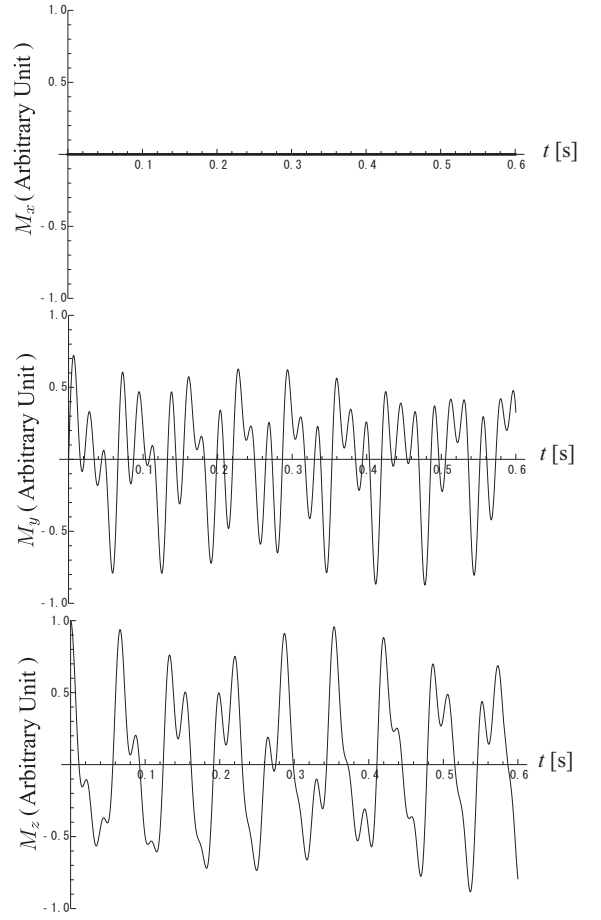


FIG. 1: Ideal dynamics of the expectation values $M_k(t)$ ($k = x, y, z$) of spin 1 when the initial state is a thermal state. Parameters $\omega_{1i}/(2\pi) = 27$ Hz, $J_{12}/(2\pi) = 53.8$ Hz, and $J_{23}/(2\pi) = 34.8$ Hz are employed in Eq. (2).

III. EXPERIMENT

We employ a linearly aligned three-spin molecule for demonstrating a Hamiltonian tomography through an edge spin. Our task is to determine the scalar coupling constants J_{12} between spins 1 and 2 and J_{23} between spins 2 and 3 by measuring only spin 1.

A. Sample and Spectrometer

We demonstrate a Hamiltonian tomography of a spin system with NMR. We employ a JEOL ECA-500 NMR spectrometer [12], whose hydrogen Larmor frequency is approximately 500 MHz. We apply weak rf-fields to generate transverse fields in the rotating frame of each spin.

A 0.3 ml, 0.78 M sample of ^{13}C -labeled L-alanine (98% purity, Cambridge Isotope) solved in D_2O , capsulated in a susceptibility matched NMR test tube [13], is used. Three ^{13}C atoms are linearly aligned in L-alanine. We label the carboxyl carbon spin 1, the α carbon spin 2,

and the methyl carbon spin 3.

The scalar coupling constants are estimated from the spectrum obtained by Fourier transforming the free induction decay (FID) signal after a hard $\pi/2$ -pulse is applied for readout [9]. Here, protons are decoupled using a standard heteronucleus decoupling technique (WALTZ-16) [14]. The information extracted from the spectrum is summarized as follows. The Larmor frequency differences are $(\omega_{02}-\omega_{01})/2\pi = 15.8$ kHz and $(\omega_{03}-\omega_{02})/2\pi = 4.4$ kHz, where ω_{0i} denotes the Larmor frequency of the spin i , for which the chemical shift is considered. Large differences in the Larmor frequencies compared with the scalar coupling constants justify the weak-coupling assumption made when the Hamiltonian (2) is introduced. The scalar coupling constant J_{13} between spins 1 and 3 is on the order of 1 Hz [15], which is much smaller compared to J_{12} and J_{23} , and hence we can safely ignore it in our analysis. As a result, the Hamiltonian of alanine molecule is well approximated by Eq. (2).

Measured relaxation times are $T_1(1) = 15.5$ s, $T_1(2) = 1.4$ s, $T_1(3) = 0.9$ s and $T_2(1) = 0.45$ s, $T_2(2) = 0.23$ s, $T_2(3) = 0.63$ s, where the argument labels the spin. The spin 2 has the shortest T_2 . In view of the fact that our data acquisition time to estimate the Hamiltonian is much shorter than any of $T_1(i)$, we ignore the effect of T_1 from now on. In contrast, we fully take the effect of $T_2(i)$ into account in our numerical calculations.

The transverse fields are applied to spins by feeding oscillating currents with three different frequencies, corresponding to the Larmor frequencies of the spins, to the coil. Their strengths are characterized by ω_{1i} .

B. Transverse Field Calibration

We measure the dynamics of spin 1 in the presence of $\omega_{11}/(2\pi) = 27$ Hz only, while other ω_{1i} ($i = 2, 3$) is set to 0, as shown in Fig. 2. The data was acquired in every 0.004 s for $0 \leq t \leq 0.6$ s. The periodicity provides the information on the strength of the transverse fields, while the decay rate is determined by the relaxations and the field inhomogeneities. We find that the relaxations only are not enough to reproduce the decay, as demonstrated by the dashed line in Fig. 2. Both relaxations and field inhomogeneities must be considered to reproduce the decay rate. We obtain the variance $\sigma/\omega_{1i} = 0.05$ in Eq. (5) by fitting the data.

C. Results

We measure the dynamics of spin 1 in two cases.

In Case 1, the initial state is thermal and the transverse fields $\omega_{1i}/(2\pi) = 27$ Hz are applied to all the spins. The dynamics of the expectation values M_x , M_y , and M_z of spin 1 are shown in Fig. 3 as functions of time t . In Fig. 3, we see there are structures different from a simple

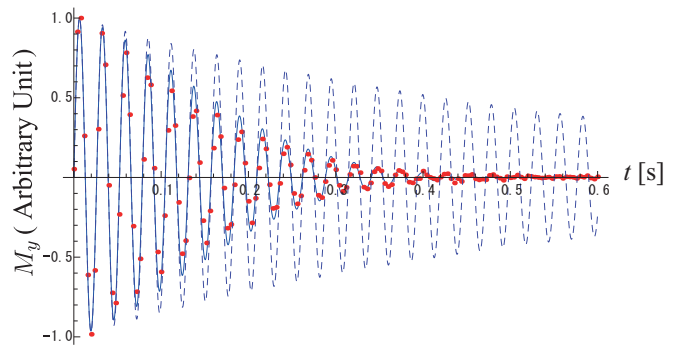


FIG. 2: (Color online) Calibration of strength and inhomogeneity of transverse field. Experimental results with a setting given in the text are shown. The dashed line shows the numerical result in which only the effect of relaxation is taken into account, while the solid line is the result in which both relaxations and inhomogeneities of transverse fields are considered.

sinusoidal oscillation which is expected without interactions. In other words, we obtain information concerning the interactions by measuring spin 1 only. It should be noted, however, that the spin dynamics is strongly affected by relaxations and transverse field inhomogeneities of all spins.

In Case 2, we have chosen $\omega_{11} = 0$, $\omega_{12}/(2\pi) = \omega_{13}/(2\pi) = 27$ Hz. Since $\omega_{11} = 0$, we would not expect any dynamics in spin 1 if a thermal state were employed as an initial state. To avoid this problem, the initial state of spin 1 is prepared by applying a $\pi/2$ -pulse along the y -axis to the thermal equilibrium state, while the initial states of spins 2 and 3 remain thermal. We again obtain the information on the interactions by measuring only spin 1 as shown in Fig. 4.

IV. ESTIMATION OF COUPLING CONSTANTS

In this section, we pretend as if we do not know the coupling constants J_{12} and J_{23} and, instead, we estimate them by fitting numerically evaluated $\langle I_k^1(t) \rangle$ with various values of (J_{12}, J_{23}) to the experimental data. Although we defined the magnetization $M_k(t)$ of the first spin as the expectation value $\langle I_k^1(t) \rangle$, we temporarily assign $M_k(t)$ to the experimental data while $\langle I_k^1(t) \rangle$ to the corresponding numerical result to avoid confusion. Let us define the “distance” between the experimental data $M_k(t)$ and the numerical result $\langle I_k^1(t) \rangle$ by

$$D_k(J_{12}, J_{23}) = \sqrt{\sum_j |\langle I_k^1(t_j, J_{12}, J_{23}) \rangle - M_k(t_j)|^2}.$$

Here $\{t_j\}$ denotes the set of data acquisition points and $\langle I_k^1(t_j, J_{12}, J_{23}) \rangle$ is the numerically evaluated expectation value of the k th component of spin 1 at time t_j with the

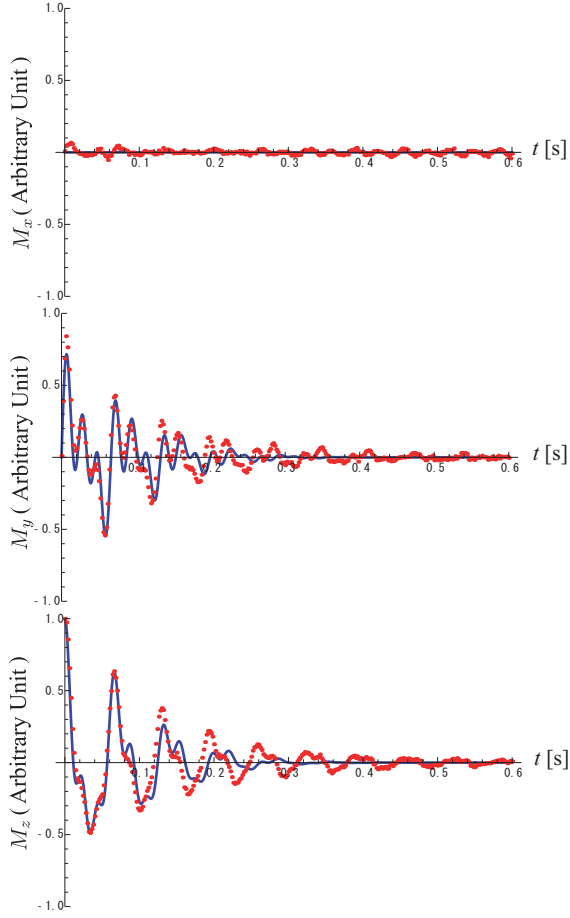


FIG. 3: (Color online) Dynamics of M_x , M_y , and M_z of spin 1 are shown for Case 1, when all $\omega_{1i}/(2\pi) = 27$ Hz and the initial states of all spins are thermal. Experimental Results are shown by dots, and the solid lines are the numerical results, in which known values of coupling constants are employed.

coupling constants (J_{12}, J_{23}). In actual experiment, data was acquired in every 0.002 s for $0 \leq t \leq 0.6$ s.

We do not make use of the spectra obtained by the Fourier transforms of time domain signals since the time window is not large enough to provide sharp peaks in the spectra. We can freely select the fitting window from $t = 0$ to $t_w > t_0$, where $t_0 = 2\pi/J_{12} + 2\pi/J_{23} \sim 50$ ms is the minimum time required for information to propagate from spin 1 to spin 3 through spin 2 and then propagate back to spin 1. Clearly there is an optimal value for t_w , since too small t_w provides too little data to be fitted, while too large t_w makes relaxations and field inhomogeneities too significant. We estimate the coupling constants for three different values of t_w and compare the results in the following.

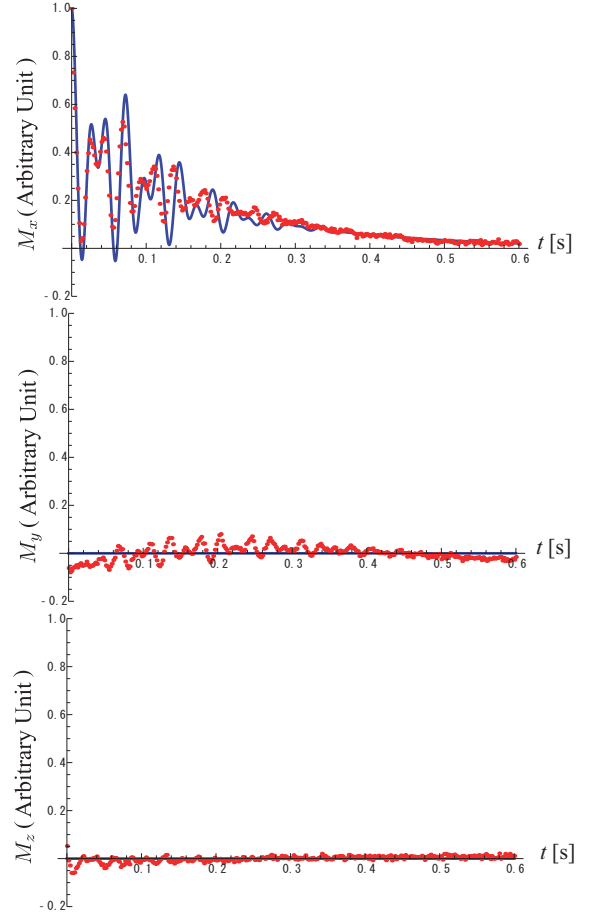


FIG. 4: (Color online) Dynamics of M_x , M_y , and M_z of spin 1 are shown for Case 2, when $\omega_{11} = 0$ and $\omega_{12}/(2\pi) = \omega_{13}/(2\pi) = 27$ Hz. The initial state of spin 1 is prepared by applying a $\pi/2$ -pulse along the y -axis to the thermal state, while those of spin 2 and 3 remain thermal. Experimental results are shown by dots, and the solid lines show the numerical results, in which known values of coupling constants are used.

A. Case 1: $\omega_{11} \neq 0$

In this case, the initial states of the three spins are prepared in thermal states and transverse fields $\omega_{1i}/(2\pi) = 27$ Hz ($i = 1, 2, 3$) are applied to all three spins.

3D and contour plots of the distances $D_y(J_{12}, J_{23})$ and $D_z(J_{12}, J_{23})$ with $t_w = 0.05$ s are shown in Fig. 5 and Fig. 6, respectively. As expected, clear minima are found in these plots.

We obtain the set (J_{12}, J_{23}) that minimizes $D_y(J_{12}, J_{23})$ and $D_z(J_{12}, J_{23})$ for different $t_w = 0.05, 0.1, 0.2$ s. They are summarized in Table I.

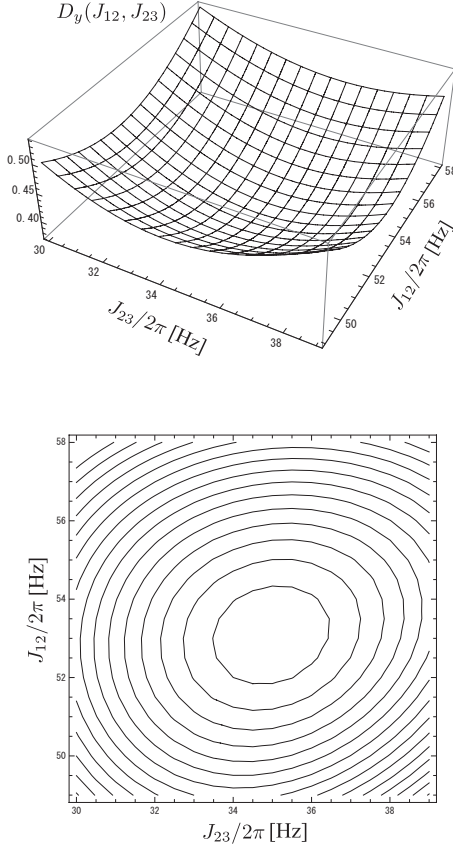


FIG. 5: 3D and contour plot of $D_y(J_{12}, J_{23})$ for Case 1 when $t_w = 0.05$ s. A clear minimum can be seen. The distance between two neighboring contours in the contour plot is 0.01.

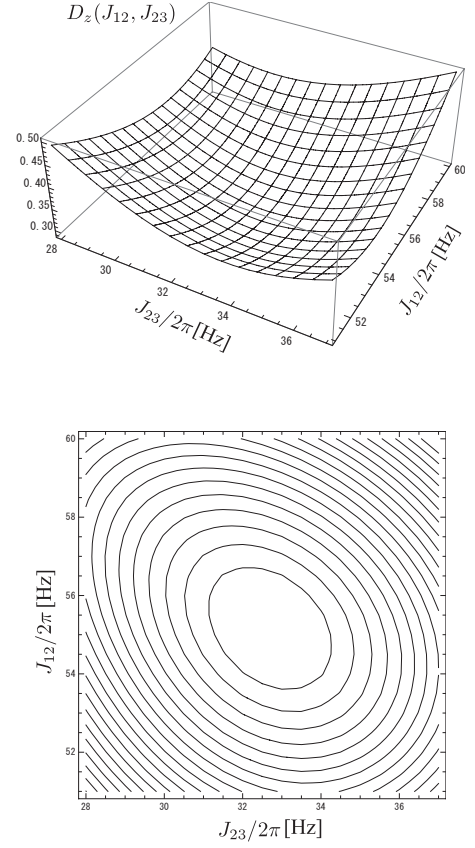


FIG. 6: 3D and contour plot of $D_z(J_{12}, J_{23})$ for Case 1 when $t_w = 0.05$ s. A clear minimum can be seen. The distance between two neighboring contours in the contour plot is 0.01.

TABLE I: Estimated coupling constants in Case 1 for various window size t_w .

Case 1	t_w [s]	$J_{12}/2\pi$ [Hz]	$J_{23}/2\pi$ [Hz]
Known values		53.8	34.8
D_y	0.05	53	35
	0.1	55.5	36
	0.2	55.5	36.5
D_z	0.05	55	33
	0.1	54.5	30.5
	0.2	56.5	25.5

B. Case 2: $\omega_{11} = 0$

We take $\omega_{11} = 0$ and $\omega_{12}/(2\pi) = \omega_{13}/(2\pi) = 27$ Hz in Case 2. To introduce nontrivial spin dynamics to spin 1, a $\pi/2$ -pulse along the y -axis, $Y = \exp(-i\pi I_y^1/2)$, is applied to spin 1 at $t = 0$ after the thermal state has been prepared.

Figure 7 shows the 3D and contour plots of the distance $D_x(J_{12}, J_{23})$ with $t_w = 0.05$ s. As expected, a unique minimum can be found in the figure.

We obtain the pair (J_{12}, J_{23}) that minimizes the dis-

tance $D_x(J_{12}, J_{23})$ with different time windows $t_w = 0.05, 0.1, 0.2$ s. Table II summarizes the results.

TABLE II: Estimated coupling constants in Case 2 for different window size t_w .

Case 2	t_w [s]	$J_{12}/2\pi$ [Hz]	$J_{23}/2\pi$ [Hz]
Known values		53.8	34.8
D_x	0.05	56.5	37.5
	0.1	58	38
	0.2	59	38.5

C. Estimation

Regardless of the choice of t_w or (D_x, D_y, D_z) , the estimated pair (J_{12}, J_{23}) is consistent with each other both in Cases 1 and 2. It seems, however, that the smallest $t_w = 0.05$ s yields the best results when we compare them with the known (J_{12}, J_{23}) obtained by different means. We have also confirmed that a smaller value, $t_w = 0.02$ s, is not large enough to estimate the coupling constants reliably as shown in Fig. 8, where the profile has a sharp

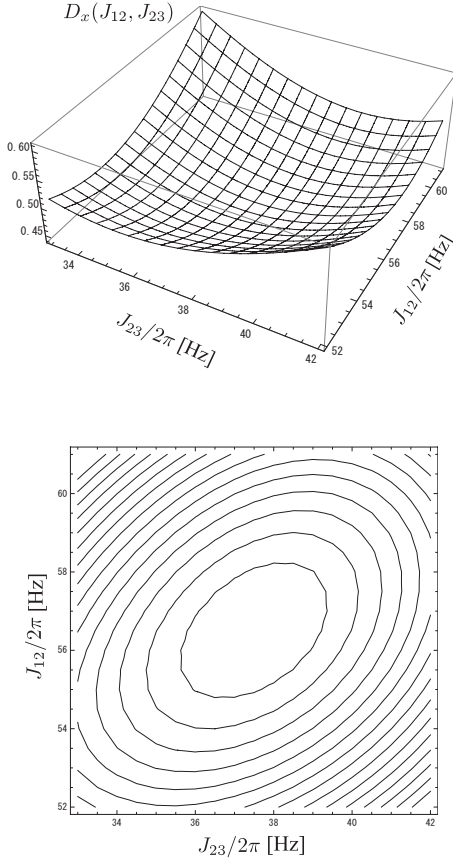


FIG. 7: 3D and contour plots of $D_x(J_{12}, J_{23})$ for Case 2 with time window $t_w = 0.05$ s. A clear minimum can be seen. The distance between two neighboring contours in the contour plot is 0.01.

minium along the J_{12} -direction but is almost flat along the J_{23} -direction. This behavior clearly shows the significance of the time $t_0 \sim 0.05$ s defined previously. The effect of J_{23} does not manifest itself yet in the behavior of spin 1 for a short time less than t_0 . On the other hand, for $t_w \sim t_0$, relaxation and field inhomogeneity are less serious yet, and the data produces an excellent result, while the results provided by a larger t_w suffer from these effects.

V. SUMMARY

We have successfully demonstrated for the first time that indirect Hamiltonian tomography is possible in NMR setup. As long as the system is small enough for efficient data fitting, the estimated values are surprisingly close to the real ones, given the substantial amount of noise and inhomogeneities in the system. This paves the way towards the identification of spins and couplings which are off-resonant or would usually be drowned by background noise. While the methods of [5, 8] rely on Fourier analysis, which is only applicable in systems

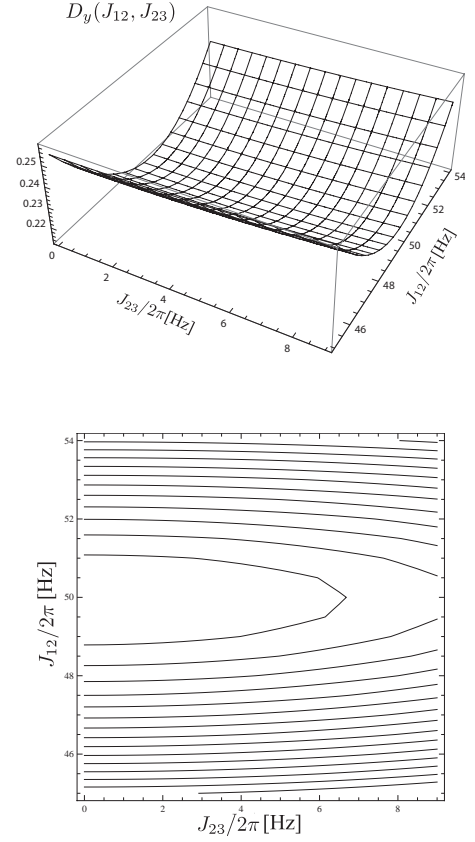


FIG. 8: 3D and contour plots of $D_y(J_{12}, J_{23})$ for Case 1 with time window $t_w = 0.02$ s. It shows that the time is not large enough to estimate the coupling constant J_{23} . The distance between two neighboring contours in the contour plot is 0.0028.

clean enough for sufficiently long time data acquisition, our method can be applied in more noisy cases.

We have shown that there is a competition in the observed evolution between amount of data acquired and the amount of noise coming in. It seems optimal to choose rather short data acquisition times in order to get a good agreement of the estimated couplings with their real values.

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